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- (54) [Title of the Invention]: **Process for the Production of Bis[2-(N,N-dimethylamino)-ethyl]ether**
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SPECIFICATION

1. Title of the Invention

Process for the Production of Bis[2-(N,N-dimethylamino)ethyl]ether

2. Claims

1. A process for the production of bis[2-(N,N-dimethylamino)ethyl]ether, characterized in that diethylene glycol or 2-[2-(N,N-dimethylamino)ethoxy]ethanol is reacted with

dimethylamine at a temperature of from approximately 150 to 300°C in the presence of hydrogen using a copper-based catalyst in a closed vessel, and the secondary amino compound generated as part of the byproducts is then methylated.

3. Detailed Description of the Invention

The present invention relates to a safe, economical, improved process for the production of bis[2-(N,N-dimethylamino)ethyl]ether (abbreviated hereinafter as BDMEE).

BDMEE is a useful compound employed as a catalyst to produce polyurethane foam from organic isocyanate and polyol. Many methods of producing the compound, such as the following, have consequently been developed up to now. Specifically, the methods include production via a methochloride of BDMEE from bis[2-(chloroethyl)]ether and trimethylamine (UP Patents Nos. 3,400,157 and 3,426,072), production from 2-(N,N-dimethylamino)ethyl chloride and sodium 2-(N,N-dimethylamino)ethoxide (US Patent No. 3,480,675), production from sodium 2-(N,N-dimethylamino)ethoxide and SO₃ gas (US Patent No. 4,247,482), and production from sodium 2-(N,N-dimethylamino)ethoxide and 2-(N,N-dimethylamino)ethanol in the presence of a sulfur oxychloride (US Patent No. 4,177,212).

However, when a chlorine compound or sulfur compound is used in the raw material, there is a risk of causing corrosion of the equipment and also the drawback of generating large quantities of chlorides and sulfates that require complicated disposal treatment.

There is also a method of production from 2-[2-(N,N-dimethylamino)ethoxy]ethanol (abbreviated hereinafter as DMEE) and trimethylamine in the presence of metallic nickel (US Patent No. 3,957,875). However, it is difficult to call this method an industrially satisfactory production process because the catalyst is expensive, the reaction takes a long time, and BDMEE cannot be obtained at a satisfactory yield unless a three-fold or greater molar quantity of trimethylamine is used in relation to the raw material DMEE.

Therefore, an easy, safe, economical production process has been desired.

As a result of in-depth research, the present inventors attained the present invention by discovering that diethylene glycol and DMEE react easily with dimethylamine at a good yield in

the presence of a copper-based catalyst. The process of the present invention is a novel, economically valuable method.

The process of the present invention is characterized in that diethylene glycol or DMEE with dimethylamine are reacted at a temperature of from approximately 150 to 300°C in the presence of a copper-based catalyst and hydrogen in a closed vessel, and the secondary amino compound generated as a part of the byproducts is then methylated to produce BDMEE.

The process of the present invention is ordinary liquid-phase batch production. However, continuous production can also be made possible by selecting the appropriate equipment.

When implementing the process of the present invention, the raw material alcohol, amine, and catalyst are mixed in a suitable container and the reaction progresses easily by heating in the presence of hydrogen gas. A closed container is used to keep the raw material amine in the liquid phase.

Examples of an appropriate copper catalyst to use in the process of the present invention include a Raney copper catalyst, reduced copper catalyst, and copper-chromium catalyst. About 0.2-20 % by weight in relation to the raw material alcohol is effective as the amount used. Usually, 1-5 % by weight is used.

The reaction progresses smoothly at a temperature of approximately 150-300°C. A temperature of about 200-250°C is particularly preferred because of considerations that include economic efficiency.

Elevation of the internal pressure by the amine as the reaction temperature rises is seen since the reaction is conducted in a closed apparatus, as mentioned above. This can be regulated as is appropriate by the quantity of charge introduced into the container. Reacting at a pressure of approximately 50-130 kg/cm² is usually preferred because of considerations that include operability and safety.

The process of the present invention is appropriately carried out in an inert gas atmosphere that does not negatively affect the reactions, e.g., in a hydrogen gas atmosphere or a nitrogen gas atmosphere in the presence of hydrogen gas. Conducting [the reaction] in a

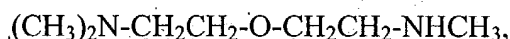
hydrogen gas atmosphere is especially preferred from the viewpoints of maintaining the desired reaction efficiency and catalyst activity.

Although the reaction of the process of the present invention progresses with stoichiometric quantities of raw material compounds, it is usually preferred that the amount of dimethylamine used in relation to the diethylene glycol and DMEE be an excess over the respective reaction equivalents, i.e., approximately 3-4 mol per mole of diethylene glycol and approximately 1.5-2 mol per mole of DMEE.

Reaction conditions such as the above are preferred for suppressing secondary reactions and raising the conversion rate.

When diethylene glycol is used as the raw material in the process of the present invention, DMEE is recovered as an intermediate. This can then be used as a raw material to produce BDMEE.

When the process of the present invention is implemented, the only byproducts generated are N-methylmorpholine, a secondary amino compound of the formula



and a very high-boiling compound of undetermined structure, without any of the aforementioned byproducts that require complicated disposal treatment being generated. After the amination reaction has been completed and the catalyst recovered by filtering the reactants, the unreacted dimethylamine is recovered by distillation. BDMEE is then obtained by fractional distillation subsequent to a methylation reaction, e.g., after methylating the secondary amino compound by the formic acid-formalin method.

Since it is difficult to separate the secondary amino compound and BDMEE, conversion into the target compound can be easily accomplished by further submitting the reaction mixture to a methylation reaction, and BDMEE can be obtained at a high yield.

The process of the present invention will be explained concretely below by working examples. However, the present invention is not limited by these examples. "Parts" in the working examples means "parts by weight."

Working Example 1

Three hundred parts (2.25 mol) of 2-[2-(N,N-dimethylamino)ethoxy]ethanol (DMEE), 180 parts (3.99 mol) of dimethylamine, and 15 parts of a copper-chromium catalyst [made by Nikki Chemical: N-203] were placed in a 1000-mL autoclave equipped with a stirrer. After being sparged with nitrogen, the vessel was pressurized to 10 kg/cm² by hydrogen and heated under stirring.

After reacting for ten hours near a temperature of 225-235°C and pressure of 60-67 kg/cm², the catalyst was recovered by filtering the reaction mixture. Gas chromatographic analysis of the filtrate showed 64.0 parts of residual DMEE (conversion rate 78.7%), 155.5 parts of bis[2-(N,N-dimethylamino)ethyl]ether (BDMEE) (selectivity 54.7%), 25.0 parts of byproduct N-methylmorpholine, and a small amount of secondary amino compound. After the dimethylamine was recovered by distillation, 10.2 parts of p-formaldehyde and 15.5 parts of formic acid were added, the ingredients were heated for two hours at 118°C, and the secondary amino compound was converted into BDMEE. [The product] was neutralized by 5.2 parts of 50% sodium hydroxide aqueous solution. The oily part of the supernatant that separated into two layers was taken and fractionally distilled in a 15-level rectifying column to obtain 150 parts of BDMEE (selectivity 52.8%) of b₁₀₀ 120.5°C.

Working Example 2

Three hundred parts (2.25 mol) of DMEE, 200 parts (4.44 mol) of dimethylamine, and 15 parts of a Raney copper catalyst were reacted for nine hours at a temperature of 230°C and a pressure of 60-70 kg/cm² in the same procedure as in working example 1. Gas chromatographic analysis of the reaction solution found 111 parts of residual DMEE (conversion rate 63.0%), 124 parts of BDMEE (selectivity 54.5%), and 15 parts of N-methylmorpholine.

Working Example 3

Two hundred parts (1.89 mol) of diethylene glycol, 335 parts (7.43 mol) of dimethylamine, and 10 parts of a copper-chromium catalyst were supplied in the same procedure as in working example 1 and reacted for 15.5 hours at a temperature of 230°C and a pressure of 133-135 kg/cm². Gas chromatographic analysis of the reaction solution found 1.5 parts of

residual diethylene glycol (conversion rate 99.2%), 117.7 parts of BDMEE (selectivity 39.3%), 58.1 parts of DMEE (selectivity 23.3%), and 27.7 parts of N-methylmorpholine.

Working Example 4

Two hundred parts (1.89 mol) of diethylene glycol and 20 parts of basic copper carbonate $[\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}]$ were supplied in the same procedure as in working example 1 and reduced for two hours at 165°C by capping with hydrogen, yielding a metallic copper catalyst. After cooling, 200 parts (4.44 mol) of dimethylamine was supplied. After being sparged with nitrogen and pressurized to 10 kg/cm² with hydrogen, [the contents] were reacted for 10 hours at a temperature of 250°C and a pressure of 80-97 kg/cm². Gas chromatographic analysis of the reaction solution found 6 parts of residual diethylene glycol (conversion rate 97%), 67 parts of BDMEE (selectivity 22.9%), 80 parts of N-methylmorpholine, and 39 parts of DMEE (selectivity 16.0%).

Reference Example

Two hundred parts (1.89 mol) of diethylene glycol, 240 parts (5.32 mol) of dimethylamine, and 10 parts of a Raney nickel catalyst were supplied in the same procedure as in working example 1 and reacted for five hours at a temperature of 230°C and a pressure of 78-80 kg/cm². Gas chromatographic analysis of the reaction solution found 40 parts of residual diethylene glycol (conversion rate 80%) and a trace of BDMEE.

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